

# Influence of preparation method on performance of Cu(Zn)(Zr)-alumina catalysts for the hydrogen production via steam reforming of methanol

Sanjay Patel · K.K. Pant

© Springer Science + Business Media, LLC 2006

**Abstract** The selective production of hydrogen via steam reforming of methanol (SRM) was performed using prepared catalysts at atmospheric pressure over a temperature range 200–260°C. Reverse water gas shift reaction and methanol decomposition reactions also take place simultaneously with the steam reforming reaction producing carbon monoxide which is highly poisonous to the platinum anode of PEM fuel cell, therefore the detailed study of effect of catalyst preparation method and of different promoters on SRM has been carried out for the minimization of carbon monoxide formation and maximization of hydrogen production. Wet impregnation and co-precipitation methods have been comparatively examined for the preparation of precursors to Cu(Zn)(Al<sub>2</sub>O<sub>3</sub>) and Cu(Zn)(Zr)(Al<sub>2</sub>O<sub>3</sub>). The catalyst preparation method affected the methanol conversion, hydrogen yield and carbon monoxide formation significantly. Incorporation of zirconia in Cu(Zn)(Al<sub>2</sub>O<sub>3</sub>) catalyst enhanced the catalytic activity, hydrogen selectivity and also lower the CO formation. Catalyst Cu(Zn)(Zr)(Al<sub>2</sub>O<sub>3</sub>) with composition Cu/Zn/Zr/Al:12/4/4/80 prepared by co-precipitation method was the most active catalyst giving methanol conversion up to 97% and CO concentration up to 400 ppm. Catalysts were characterized by atomic absorption spectroscopy (AAS), Brunauer-Emett-Teller (BET) surface area, pore volume, pore size and X-ray powder diffraction (XRPD). The XRPD patterns revealed that the addition of

zirconia improves the dispersion of copper which resulted in the better catalytic performance of Cu(Zn)(Zr)(Al<sub>2</sub>O<sub>3</sub>). The time-on-stream (TOS) catalysts stability test was also conducted for which the Cu(Zn)(Zr)(Al<sub>2</sub>O<sub>3</sub>) catalyst gave the consistent performance for a long time compared to other catalysts.

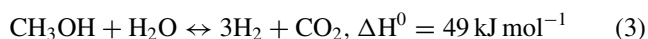
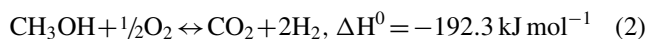
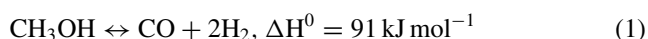
**Keywords** Cu(Zn)(Zr)(Al<sub>2</sub>O<sub>3</sub>) · Co-precipitation · Hydrogen

## 1. Introduction

The polymer electrolyte membrane (PEM) fuel cells are currently the leading candidate for the commercial transportation exploitation of fuel cell technology, which emits lower amount of pollutants and offers higher efficiencies compared to internal combustion engines. PEM fuel cells convert the hydrogen in to useful electric power with an efficiency that is not limited by the thermodynamics. Due to current infrastructure, storage technology and safety concerns, hydrogen cannot be stored on-board in adequate amount for the mobile applications. Therefore, on demand, reforming of liquid hydrocarbons to produce hydrogen is seen as an attractive means of providing the necessary hydrogen to the fuel cell. On board methanol reforming to produce hydrogen has a couple of advantages over other potential fuels: unlike gasoline or diesel fuel, liquid methanol can be produced from biomass, can be adapted easily to the current infrastructure, can be stored easily and finally it has a high hydrogen to carbon ratio [1–4]. The hydrogen can be produced from methanol according to three different processes: methanol decomposition (MD: Eq. 1), partial oxidation of methanol (POM: Eq. 2) and steam reforming of methanol (SRM: Eq. 3).

S. Patel · K.K. Pant (✉)  
Department of Chemical Engineering, Indian Institute of Technology-Delhi, Hauz Khas, New Delhi-110016, India  
e-mail: kkpant@chemical.iitd.ac.in

S. Patel  
Department of Chemical Engineering, Institute of Technology,  
Nirma University of Science and Technology,  
Ahmedabad-382481, India



Unfortunately, the MD and POM produce considerable amount of CO as a by-product. On the other hand, SRM can produce significantly low CO and H<sub>2</sub>/CO<sub>2</sub> in the molar ratio of 3/1. Widely used catalysts for generating hydrogen from SRM are copper based catalysts [5–8]. Their activity is greatly dependent on the dispersion of copper and high copper dispersion is desirable. However, the current catalysts produce relatively a high concentration of CO than the upper limit of CO concentration in feed gas for the PEM fuel cells, and also facing the problem of deactivation [5, 8–11]. Therefore in the present study efforts have been made to improve the catalytic activity and stability by the addition of zirconia promoter and by finding out the effective catalyst preparation method. We performed the SRM over Cu(Zn)(Al<sub>2</sub>O<sub>3</sub>) and Cu(Zn)(Zr)(Al<sub>2</sub>O<sub>3</sub>) catalysts prepared by wet impregnation and co-precipitation methods. We found that the combination of catalyst preparation by co-precipitation method and addition of zirconia in Cu(Zn)(Al<sub>2</sub>O<sub>3</sub>) catalysts, improved the catalyst activity and stability greatly for the steam reforming of methanol.

## 2. Experimental

### 2.1. Catalyst preparation

#### 2.1.1. Wet impregnation

The excess solutions of copper nitrate Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, zinc nitrate Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and zirconium oxynitrate ZrO(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O precursors were made by dissolving them in a sufficient quantity of double distilled water to prepare the Cu(Zn)(Zr)(Al<sub>2</sub>O<sub>3</sub>) catalysts designated as WiCZZrA; i = 1, 2. Alumina pellets were dipped in the solution for 4 h under vigorous stirring. The pH of the mixture was maintained at 7. The excess water was removed in a rotary vacuum evaporator. Then impregnated wet pellets were dried for 12 h at 125°C followed by a calcination, to convert nitrates in to oxides, in the presence of air at 400°C for 4 h. The same procedure was followed to prepare the WiCZA; i = 1, 2 catalysts.

#### 2.1.2. Co-precipitation

Cu(Zn)(Zr)(Al<sub>2</sub>O<sub>3</sub>) catalysts designated as PiCZZrA; i = 1, 2, 3 were prepared by the co-precipitation method as following. The 1.25 M molar solutions of Cu, Zn, ZrO and

Al nitrates were prepared separately and then mixed. 0.5 M Na<sub>2</sub>CO<sub>3</sub> solution was added drop wise to the nitrate solution under vigorous stirring. The pH of mixture was maintained at 7 and temperature was at 70°C. Precipitates aged for 1 h followed by removal of the filtrate. Precipitates were washed three times by double distilled water to remove Na<sup>+</sup> and any remaining salts. Then precursors were dried for 12 h at 110°C, crushed to a fine powder, and calcined. Calcinations were carried out in the presence of air at 400°C for 4 h. Pellets, 3 mm size, of fine powder were made in an automatic palletizing press Techno Search AP-15. The pellets were crushed and sieved to a desired particle size. Cu(Zn)(Al<sub>2</sub>O<sub>3</sub>) catalysts designated as PiCZA; i = 1, 2, 3 were also prepared by the same procedure.

### 2.2. Catalysts characterization

The final composition of the catalysts was determined by atomic absorption spectroscopy (AAS) Varian AA420FS. Prior to analysis, samples were prepared by dissolving catalyst in the nitric acid, followed by dilution with double distilled water to a concentration within the detection range of the instrument. Calibration solutions were prepared by dissolving the corresponding metal salts in double distilled water. The BET surface area and the pore structure of the catalysts were characterized by nitrogen adsorption at –196°C on ASAP 2010, Micromeritics. Each sample was degassed at 200°C under vacuum for 4 h before measurement. Specific surface areas were calculated using a value of 0.162 nm<sup>2</sup> for the cross-sectional area of the nitrogen molecule using BET model. The volume of nitrogen adsorbed due to the micro porosity was determined from the positive intercept on the adsorbed volume axis of the t-plot. Different crystalline phases present in the catalysts were identified by X-ray powder diffraction (XRPD) using the Philips X'PERT PW1827/21 powder diffractometer. The monochromatic radiation Cu-Kα 1.5418 Å was applied and data obtained for the diffraction angle ranging from 10–60°.

### 2.3. Catalytic activity

Catalysts performance was evaluated in a fixed-bed stainless steel reactor (19 mm i.d.). SRM reaction was carried out at an atmospheric pressure by placing the reactor in an electric furnace consisting of two heating zones equipped with two PID temperature controllers. A thermocouple was placed at the center of catalyst bed to monitor the reactor temperature. Catalysts were tested in an integral mode at different reaction temperatures and contact-times under plug flow conditions. Isothermal conditions were maintained in the central catalytic zone of the reactor. Intra particle diffusion was minimized by selecting the particle size 0.6–0.8 mm based on preliminary runs. Prior to SRM reaction catalysts

were exposed to a reduction environment to reduce copper oxide to the copper. The reduction was carried out in-situ using a stream of 10% hydrogen in nitrogen at a temperature ramp of  $5^{\circ}\text{C min}^{-1}$  and dwelling at  $240^{\circ}\text{C}$  for 2 h. For a typical run, the experimental procedure followed is as following. Liquid methanol and water using peristaltic pumps were passed separately to a preheater maintained at  $220^{\circ}\text{C}$  where reactants got vaporized and mixed. The reactants mixture fed to the reactor at desired temperature where the steam reforming of methanol reaction took place. The stream of products and unconverted species passed through a condenser and liquid-gas separator followed by sampling ports. Reaction products were analyzed by Nucon-5700 Gas chromatograph, equipped with thermal conductivity detector and carbosphere column for the gaseous product concentration measurement and flame ionization detector with silica-alumina fused capillary column for unconverted methanol concentration measurement.

### 3. Results and discussion

#### 3.1. Physicochemical properties of catalysts

The BET surface area, pore volume and pore size are listed in the Table 1. for a wide range of  $\text{Cu}(\text{Al}_2\text{O}_3)$  based catalysts promoted by  $\text{ZnO}$  and  $\text{ZrO}_2$ , and prepared by the wet impregnation and co-precipitation method. The BET surface areas of the catalysts were strongly affected by the method of catalyst preparation. The precursors impregnated

over  $\gamma$ -alumina ( $S_{\text{BET}} = 216 \text{ m}^2 \text{ g}^{-1}$ ) had a higher surface area compared to the precipitated catalysts irrespective of kind of promoter incorporated in the catalysts. PCA ( $\text{Cu}/\text{Al}:15/85$ ) had the surface area only  $46 \text{ m}^2 \text{ g}^{-1}$ , on the other hand P1CZA ( $\text{Cu}/\text{Zn}/\text{Al}:10/5/85$ ) had  $59 \text{ m}^2 \text{ g}^{-1}$  and P1CZZrA ( $\text{Cu}/\text{Zn}/\text{Zr}/\text{Al}:10/5/2/87$ ) had  $67 \text{ m}^2 \text{ g}^{-1}$ , which shows that the promoters  $\text{ZrO}_2$  and  $\text{ZnO}$  improved the catalyst surface area significantly, moreover the W1CZZrA ( $\text{Cu}/\text{Zn}/\text{Zr}/\text{Al}:8/4/2/86$ ) catalyst incorporated  $\text{ZrO}_2$  has the highest surface area  $162 \text{ m}^2 \text{ g}^{-1}$  compared to almost same alumina contained W1CZA ( $\text{Cu}/\text{Zn}/\text{Al}:10/5/85$ ) catalyst incorporating only  $\text{ZnO}$ . The above discussion suggested that the  $\text{ZrO}_2$  improved the catalyst surface area greatly, which resulted in a higher activity reported in the subsequent discussion. Table 1 shows that the actual doping of precursors was less than the initial stoichiometric composition due to attrition and heat treatment, and also filtrate carry over for the co-precipitation method. Figure 1 shows the XRPD patterns of reduced fresh and spent catalysts. On the reduction  $\text{CuO}$  reduced to the  $\text{Cu}$  while  $\text{ZnO}$  and  $\text{ZrO}_2$  remained in oxide state. The XRPD patterns of spent catalysts indicate that the presence of  $\text{ZrO}_2$  transformed the part of  $\text{Cu}$  in to  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  after the course of SRM reaction while  $\text{ZnO}$  transformed the part of  $\text{Cu}$  only in to the  $\text{CuO}$ .

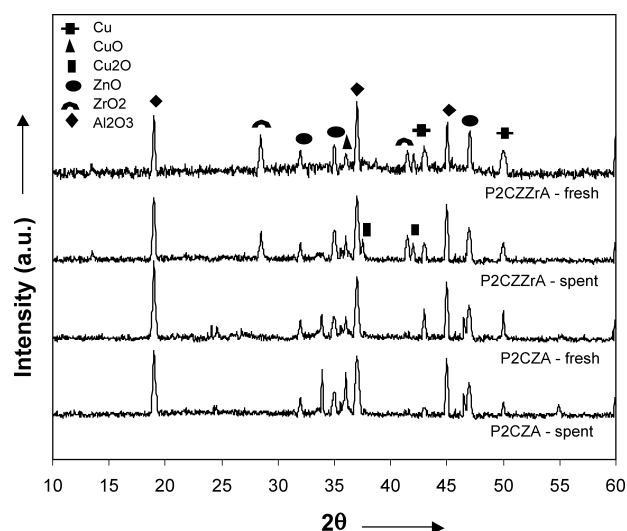
#### 3.2. Comparison of catalysts activity

Catalysts WCA ( $\text{Cu}/\text{Al}:15/85$ ) and PCA ( $\text{Cu}/\text{Al}:15/85$ ) gave very low methanol conversion and hence low hydrogen

**Table 1** Physiochemical properties of catalysts

Group	<sup>a</sup> Catalysts	Composition, mol%		$S_{\text{BET}}$ $\text{m}^2 \text{ g}^{-1}$	$V_{\text{pore}}$ $\text{cm}^3 \text{ g}^{-1}$	$D_{\text{avg}}$ $^{\circ}\text{A}$	$^b\text{X}_{\text{methanol}}$ %	$^b\text{H}_2$ rate <sup>c</sup>	$^b\text{CO}$ mol%
		Stoichiometric	Final						
		$\text{Cu}/\text{Zn}/\text{Zr}/\text{Al}$	$\text{Cu}/\text{Zn}/\text{Zr}/\text{Al}$						
A	WCA	15/0/0/85	14/0/0/86	112	0.26	47	31	81	3
	PCA	15/0/0/85	13.5/0/0/86.5	46	0.11	26	37	97	2.8
	W1CZA	10/5/0/85	9.5/4.8/0/85.7	148	0.33	61	75	198	2.3
	W2CZA	20/10/0/70	18.6/9.7/0/71.7	121	0.29	53	42	110	2.5
B	P1CZA	10/5/0/85	9.6/5.1/0/85.3	59	0.13	32	72	190	2.2
	P2CZA	20/10/0/70	20.4/10.2/0/69.4	74	0.26	41	88	233	1.9
	P3CZA	40/20/0/40	42/21/0/37	54	0.12	29	68	180	2.1
C	W1CZZrA	8/4/2/86	7.8/3.9/2/86.3	162	0.41	59	81	217	1.2
	W2CZZrA	12/4/4/80	11/3.8/3.9/81.3	153	0.37	54	60	159	1.6
D	P1CZZrA	10/5/2/87	8.5/4.1/2.2/85.2	67	0.16	36	84	225	1
	P2CZZrA	12/4/4/80	13/4.2/4.3/78.5	98	0.29	48	97	261	0.8
	P3CZZrA	20/10/5/65	22/11/6/61	71	0.18	39	89	239	0.9

<sup>a</sup>First word of designation of each catalyst represents the method of preparation used i.e. **P** represents the Co-precipitation and **W** represents the Wet Impregnation. <sup>b</sup>( $\text{W}/\text{F} = 11 \text{ kg}_{\text{cat}} \text{ mol}^{-1} \text{ s}$ ,  $T = 260^{\circ}\text{C}$ ,  $S/\text{M} = 1.4 \text{ M}$ ). <sup>c</sup> $\text{mmol s}^{-1} \text{ kg}_{\text{cat}}^{-1}$ .

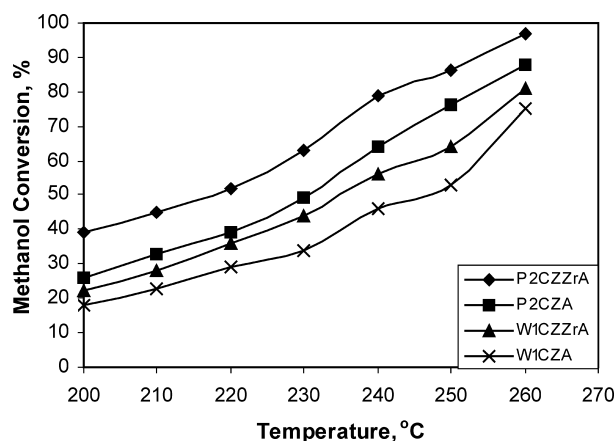


**Fig. 1** X-ray powder diffraction patterns of reduced fresh and spent catalysts

production rate as shown in Table 1, therefore promoters need to be incorporated in Cu-Al catalysts. Although the content of precursors in W1CZA (Cu/Zn/Al:10/5/85) was equal to that in P1CZA (Cu/Zn/Al:10/5/85), the conversion of methanol and the production rate of hydrogen over impregnated W1CZA were lower than those on co-precipitated P1CZA catalyst, indicating that the preparation method influences the catalyst activity. A close look to the results of each group (A-D) presented in Table 1 also suggested that the activity of  $\text{ZrO}_2$  and ZnO promoted catalysts were higher than the catalysts promoted by ZnO only, further more, the activity of each group varied with the copper loading. For each group of catalysts, the optimum loading of copper and promoters was necessary to achieve the better performance. Further detailed study of most active catalyst of each group has been carried out for the SRM process.

### 3.3. Effect of temperature on catalytic activity

Figure 2 shows the effect of temperature on the methanol conversion for the different catalysts at contact time (W/F)  $11 \text{ kg}_{\text{cat}} \text{ mol}^{-1} \text{ s}$  and steam to methanol molar ratio 1.4. The highest conversion 97% was achieved with P2CZZrA (Cu/Zn/Zr/Al:12/4/4/80) where as the lowest conversion 75% with W1CZA (Cu/Zn/Al:10/5/85) catalyst. Figure 3(a) compares the hydrogen production rate as a function of temperature for different catalysts. The hydrogen production rate for P2CZZrA catalyst increased from  $106 \text{ mmol s}^{-1} \text{ kg}^{-1}$  at  $200^\circ\text{C}$  to  $261 \text{ mmol s}^{-1} \text{ kg}^{-1}$  at  $260^\circ\text{C}$ , where as lowest hydrogen production rate  $48 \text{ mmol s}^{-1} \text{ kg}^{-1}$  was observed with W1CZA at  $200^\circ\text{C}$ . The similar trends were obtained for the hydrogen yield, mols of hydrogen produced per mols of methanol fed to the reactor, as a function of temperature (Fig. 3(b)). Catalysts prepared by co-precipitation

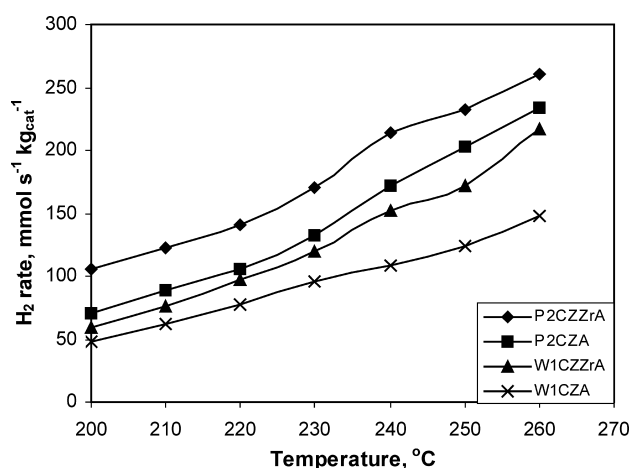


**Fig. 2** Catalysts activity comparison (W/F =  $11 \text{ kg}_{\text{cat}} \text{ mol}^{-1} \text{ s}$ , S/M = 1.4 M)

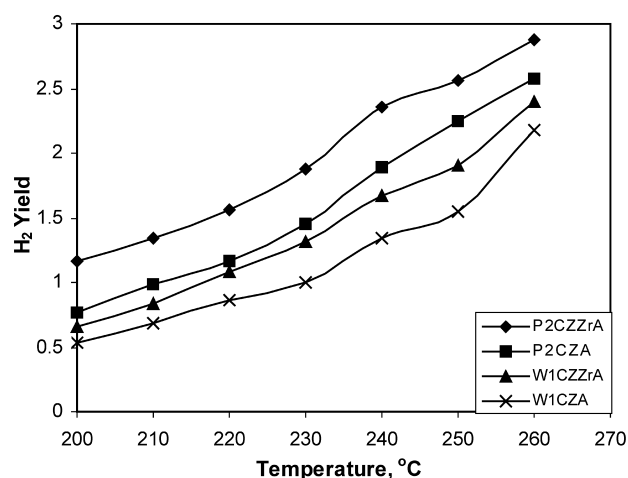
method exhibited higher activity compared to wet impregnation method, and also zirconia enhanced the catalytic activity compared to only ZnO promoted catalysts. That was due to higher surface area offered by dispersing the copper more effectively. The zirconium alone is a highly crystalline but in the presence of alumina, crystallinity of it is reduced [12]. The necessary crystallinity required for a better catalytic activity was obtained by preparing the optimum solid solutions of zirconia and alumina. For XRPD patterns as per the Scherrer formula the crystal size is inversely proportional to the peak width for a given diffraction angle and monochromatic wavelength. The peak width of copper for a P2CZZrA catalyst is broader compared to that is for P2CZA catalyst as shown in Fig. 1, which resulted in a smaller copper crystallite size. Smaller the crystallite size better the copper dispersion and more copper surface area of catalysts can be achieved which would enhance the catalyst activity.  $\text{ZrO}_2$  poses the oxygen ion vacancy that causes a geometric effect to improve the dispersion of supported copper metal particles and alter the morphology [13]. XRPD patterns of P2CZZrA catalyst also show that there is no peak for the  $\text{CuAl}_2\text{O}_4$ , which is resulted by the interaction of CuO and  $\text{Al}_2\text{O}_3$ . Therefore it can be concluded that  $\text{ZrO}_2$  promoter weaken the interaction between CuO and  $\text{Al}_2\text{O}_3$  to avoid the formation of a spinel type compound  $\text{CuAl}_2\text{O}_4$  that reduces the catalytic activity [14]. It is very well known in the literature that the catalysts containing Cu and  $\text{ZrO}_2$  behave in a bifunctional manner. Bi-functional roles of Cu and  $\text{ZrO}_2$  can also be made beneficial to change the synergy between copper and zinc to enhance the catalytic activity [15].

### 3.4. Carbon monoxide formation minimization and hydrogen selectivity

The products of the SRM over prepared catalysts were hydrogen and carbon dioxide with traces of carbon monoxide,



(a)



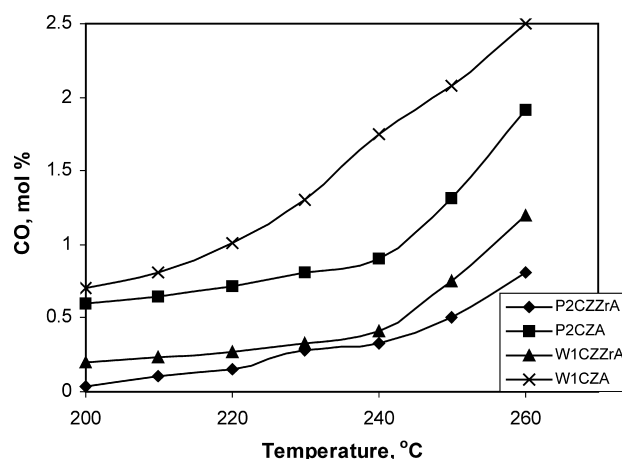
(b)

**Fig. 3** Temperature dependence of hydrogen generation ( $W/F = 11 \text{ kg}_{\text{cat}} \text{ mol}^{-1} \text{ s}$ ,  $S/M = 1.4 \text{ M}$ ) (a). Hydrogen production rate. (b). Hydrogen yield

no other compounds such as, formaldehyde [16], dimethyl ether [17], methyl formate [17], formic acid or methane were detected under the experimental conditions of this study. The CO formation was contributed by the methanol decomposition Eq. (1) and reverse water gas shift reaction (rWGS:Eq.4), which are also taking place along with the SRM (Eq. 3) reaction.



The maximum CO formation observed with the unpromoted catalysts WCA and PCA was 3 and 2.8 mol% respectively at 260°C. It can be seen from Fig. 4 that the CO formation increases as a function of temperature. Typically, W1CZA (Cu/Zn/Al:10/5/85) gave 0.7 mol% at 200°C that increased to 2.5 mol% at 260°C, and P2CZZrA (Cu/Zn/Zr/Al:12/4/4/80) gave 0.04 mol% at 200°C that

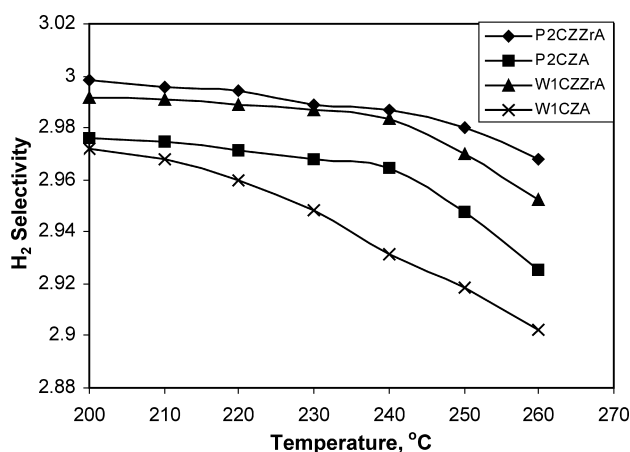


**Fig. 4** Effect of reaction temperature on CO formation ( $W/F = 11 \text{ kg}_{\text{cat}} \text{ mol}^{-1} \text{ s}$ ,  $S/M = 1.4 \text{ M}$ )

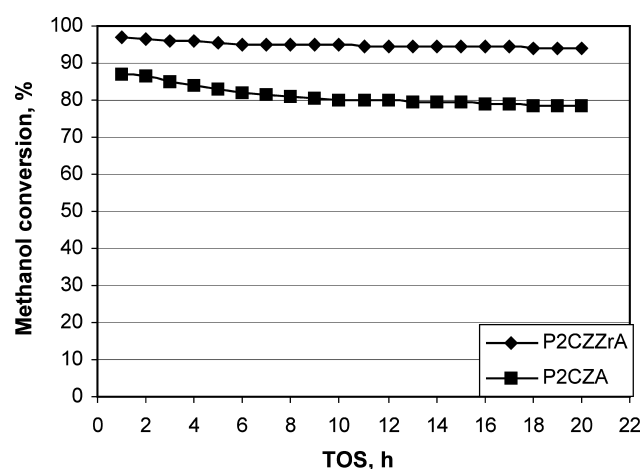
increased to 0.8 mol% at 260°C. It shows that promoter and method of preparation greatly affected the CO formation. Operating the process at low temperature and high steam to methanol ratio can also minimize the CO formation. If SRM is operated at a lower temperature the methanol conversion and corresponding hydrogen production will be less, and also the unconverted methanol has to be separated from the hydrogen rich product gas before it feed to the PEM fuel cell. That will increase the complexity of system and decrease the over all efficiency of the fuel cell system. Therefore, it is necessary to develop the catalyst, which gives high methanol conversion at low temperature that was obtained with the P2CZZrA catalyst. By providing the excess steam, the CO formation can be minimized by suppressing the rWGS reaction (Eq. 4) and also the sufficient steam will be available to the methanol during a course of SRM reaction to inhibit the MD (Eq. 1). In the present study based on our previous study [8] excess steam was supplied by keeping S/M molar ratio 1.4 for all the experiments to reduce the CO formation. The selectivity, mols of hydrogen produced per mols of methanol converted, of hydrogen decreased with temperature as shown in Fig. 5. This was because of at higher temperature MD, produces relatively less no of hydrogen mols per mol of methanol reacted; and rWGS, consumes hydrogen, got accelerated.

### 3.5. Role of zirconia in stability enhancement of catalysts

Figure 6 shows the methanol conversion as a function of time-on-stream at 260°C. The P2CZA catalyst deactivated fast by a magnitude of 9.3% over a 20 h reaction time. On the other hand the activity of P2CZZrA catalyst declined only by a magnitude of 3%. For a catalyst P2CZZrA activity declined initially and then became nearly constant most probably due to some transient transformation to a stable form under the reaction condition occurred in the catalyst, which



**Fig. 5** Influence of reaction temperature on hydrogen selectivity ( $W/F = 11 \text{ kg}_{\text{cat}} \text{ mol}^{-1} \text{ s}$ ,  $S/M = 1.4 \text{ M}$ )



**Fig. 6** Time-on-stream stability test of catalysts ( $W/F = 11 \text{ kg}_{\text{cat}} \text{ s mol}^{-1}$ ,  $T = 260^\circ\text{C}$ ,  $S/M = 1.4 \text{ M}$ )

confirms that  $\text{ZrO}_2$  is an important structural stabilizer [18]. XRPD patterns of spent P2CZZrA catalyst show that the Cu partly converted to the  $\text{Cu}_2\text{O}$  that also enhance the durability of the catalysts [19]. The reactivation of catalysts was done in an oxidative stream then again catalysts were subjected to the time-on-stream stability test. It was found that the activity partly retained compared to the fresh catalysts suggesting that the deactivation also took place because of coking.

#### 4. Conclusions

A series of  $\text{Cu}(\text{Zn})(\text{Zr})(\text{Al}_2\text{O}_3)$  and  $\text{Cu}(\text{Zn})(\text{Al}_2\text{O}_3)$  catalysts were prepared by two methods, viz. wet impregnation and co-precipitation. Through characterization revealed considerable variations in catalyst physiochemical properties

depending on the type of promoters and preparation methods used. It was found that the  $\text{Cu}(\text{Zn})(\text{Zr})(\text{Al}_2\text{O}_3)$  catalyst possessed high copper dispersion compared to  $\text{Cu}(\text{Zn})(\text{Al}_2\text{O}_3)$  catalysts to give higher catalytic activity, which was confirmed by the XRPD patterns and surface area. The catalyst preparation method also played an important role in methanol conversion, hydrogen selectivity and CO formation. Co-precipitation method exhibited higher activity compared to wet impregnation method. The addition of  $\text{ZrO}_2$  in  $\text{Cu}(\text{Zn})(\text{Al}_2\text{O}_3)$  catalysts improved the performance in terms of methanol conversion, hydrogen yield, suppression of CO formation and stability. Time-on-stream stability experiments indicated that after an initial period of deactivation, the activity of the P2CZZrA ( $\text{Cu}/\text{Zn}/\text{Zr}/\text{Al}:12/4/4/80$ ) catalyst became consistent. Therefore this catalyst is suitable, to avoid the frequent replacement of it, for the methanol reformer attached with PEM fuel cell operated vehicles.

#### References

1. J. Agrell, K. Hasselbo, K. Jansson, S.G. Jaras, and M. Boutonnet, *Applied Catalysis A: General* **211**, 239 (2001).
2. P. Mizsey, E. Newson, T. Truong, and P. Hottinger, *Applied Catalysis A: General* **213**, 233 (2001).
3. S. Velu, K. Suzuki, M. Okazaki, M.P. Kapoor, T. Osaki, and F. Ohashi, *Journal of Catalysis* **194**, 373 (2000).
4. B. Lindstrom and L.J. Pettersson, *International Journal of Hydrogen Energy* **26**, 923 (2001).
5. J.P. Shen and C. Song, *Catalysis Today* **77**, 89 (2002).
6. B. Lindstrom, J. Agrell, and L.J. Pettersson, *Chemical Engineering Journal* **93**, 91 (2003).
7. J.P. Breen and J.R.H. Ross, *Catalysis Today* **51**, 521 (1999).
8. V. Agarwal, S. Patel, and K.K. Pant, *Applied Catalysis A: General* **279**, 155 (2005).
9. H. Purnama, T. Ressler, R.E. Jentoft, H. Soerijanto, R. Schlogl, and R. Schomacker, *Applied Catalysis A: General* **259**, 83 (2004).
10. J.K. Lee, J.B. Ko, and D.H. Kim, *Applied Catalysis A: General* **278**, 25 (2004).
11. Y. Choi and H.G. Stenger, *Applied Catalysis B: Environmental* **38**, 259 (2002).
12. A. Mastalir, B. Frank, A. Szzybalski, H. Soerijanto, A. Deshpande, M. Niederberger, R. Schomacker, R. Schlogl, and T. Ressler, *Journal of Catalysis* **230**, 464 (2005).
13. W. Dow, W.Y. Wang, and T. Huang, *Journal of Catalysis* **160**, 155 (1996).
14. Li Yong-Feng, Dong Xin-Fa, and Lin Wei-Ming, *International Journal of Hydrogen Energy* **29**, 1617 (2004).
15. S. Velu, K. Suzuki, M.P. Kapoor, F. Ohashi, and T. Osaki, *Applied Catalysis A: General* **213**, 47 (2001).
16. J. Agrell, M. Boutonnet, I. Melian-Cabrera, and J.L.G. Fierro, *Applied Catalysis A: General* **253**, 201 (2003).
17. Y. Liu, T. Hayakawa, K. Suzuki, S. Hamakawa, T. Tsunoda, T. Ishii, and M. Kumagai, *Applied Catalysis A: General* **223**, 137 (2002).
18. P.H. Matter, D.J. Braden, and U.S. Ozkan, *Journal of Catalysis* **223**, 340 (2004).
19. H. Oguchi, T. Nishiguchi, T. Matsumoto, H. Kanai, K. Utani, Y. Matsumura, and S. Imamura, *Applied Catalysis A: General* **281**, 69 (2005).